New As–S Cage Structures with Organometallic Components Formed by Complex-Induced Realgar Fragmentation**

By *Henri Brunner, Bernhard Nuber, Ludwig Poll,* and *Joachim Wachter**

Dedicated to Professor Ernst Otto Fischer on the occasion of his 75th birthday

Substituent-free ligands from the elements of groups 15 and 16 are interesting primarily because of their vast structural diversity.[1, 2] Similarities exist above all in the formation of multinuclear complexes. However, the ability of P and As ligands to form ring systems is unusual; these ring systems show remarkable parallels to cyclic hydrocarbon ligands through the isolobal relationship P(As) $\leftrightarrow$ CH. Relatively little is known to date about complexes with ligands that contain elements from groups 15 and 16. A simple route to such compounds is the fragmentation of As_4S_4 with reactive transition metal complexes. Mixed realgar fragmentation products that have so far been structurally characterized are complexes with *cyclo*-As_2S,[1c] As_2S_3,[3] and As_3S_3 ligands.[4] The AsS_3 building block,[5] the first molecular example from the extensive class of sulfo salt minerals, is of particular significance.[6] Since the investigations were carried out on complexes with different structures and with various metal centers, nothing is known as yet about the fragmentation mechanism of realgar.[3, 7] We report here on the synthesis and structure determination of bi- and trinuclear Cp^xCo complexes ($Cp^x = \eta^5$-C_5Me_4Et) with AsS and As_2S_3 ligands in new modes of coordination and their reactivity relationships with one another.

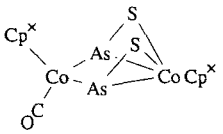
The reaction of **1** with stoichiometric quantities of As_4S_4 (toluene, 80 °C) affords complexes **2**–**5** in yields between 6 and 13%. All compounds were characterized analytically[8] and conclusions about the symmetry can be drawn from the ^{1}H NMR spectra (Table 1). X-ray structure determinations were carried out for **2** and **5**. Since the properties of **3** are very similar to those of the structurally characterized complex **6** ($Cp^* = C_5Me_5$),[3] this suggests that also in **3** a chain, in which S and As atoms alternate, bridges the two Co centers. In contrast, the structure of **4** remains open because of the numerous possible isomers.

Table 1. ^{1}H NMR spectroscopic data [a] of compounds **2**–**5**.

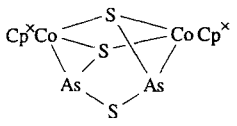
	$\delta(CH_2CH_3)$ [b]	$\delta(CH_3)$	$\delta(CH_2CH_3)$ [b]
2	0.93 (t, 3H), 1.11 (t, 3H)	1.64 (s, 6H), 1.71 (s, 6H), 1.92 (s, 6H), 1.93 (s, 6H)	2.26 (q, 2H), 2.36 (q, 2H)
3	0.95 (t, 6H)	1.65 (s, 6H), 1.66 (s, 6H), 1.75 (s, 6H), 1,76 (s, 6H)	2.27 (q, 2H), 2.28 (q, 2H)
4	0.92 (m, 6H), 1.11 (t, 3H)	1.49 (s, 3H), 1.50 (s, 3H), 1.51 (s, 3H), 1.54 (s, 3H), 1.55 (s, 3H), 1.56 (s, 3H), 1.60 (s, 3H), 1.61 (s, 3H), 1.85 (s, 3H), 1.86 (s, 3H), 1.88 (s, 6H)	2.12 (m, 4H), 2.39 (q, 2H)
5	0.95 (m, 9H)	1.47 (s, 6H), 1.49 (s, 6H), 1.52 (s, 6H), 1.57 (s, 12H), 1.60 (s, 6H)	2.10 (m, 6H)

[a] 250 MHz, $CDCl_3$, TMS int.; [b] $^3J(H,H) = 7.6$ Hz.

$[\{Cp^xCo(CO)\}_2]$ **1**



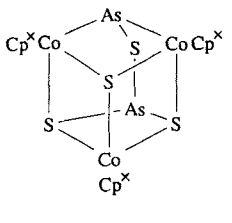
2



3

$[Cp^x_3Co_3As_4S_2]$

4



5

$[Cp^*_2Co_2As_2S_3]$ **6**

The most important feature of the crystal structure of **2**[9] is the two Co centers *syn* bridged by two η^1:η^2-AsS ligands (Fig. 1). A terminal CO group at Co2, also evident by an IR absorption at 1987 cm^{-1}, is responsible for the formal saturation of the two Co centers. The two As atoms come remarkably close to each other (2.717(2) Å),[10] whereas the S–S distance (3.278 Å) is greater than that for bonding interactions. The Co–S distances in the frameworks of **6** and **2** are the same length; of the two different Co–As distances ($\Delta = 0.08$ Å) in **2**, however, even the shorter ones are about 0.06 Å longer than those in **6**. The As–S distance (mean 2.169 Å) is about 0.07 Å shorter than that in the minerals As_2S_3 and As_4S_4[11] and other complexes which contain the η^2:η^2 AsS ligand.[7, 12]

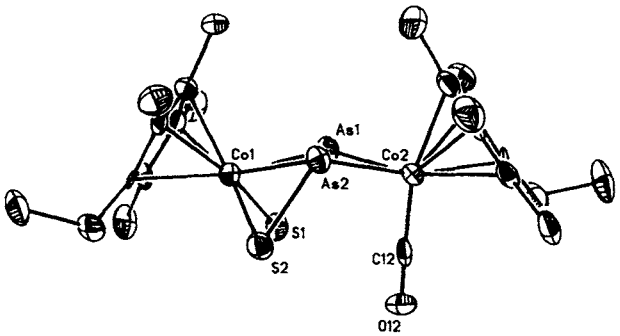


Fig. 1. Crystal structure of **2**. Selected distances [Å] and angles [°]: Co1-As1 2.473(2), Co1-As2 2.465(2), Co1-S1 2.275(4), Co1-S2 2.279(4), Co2-As1 2.383(3), Co2-As2 2.381(3), As1-S1 2.174(4), As2-S2 2.164(4), As1···As2 2.717(2), S1···S2 3.278(4); As1-Co1-As2 66.7(1), As1-Co1-S1 54.3(1), As1-Co1-S2 102.3(1), S1-Co1-S2 92.1(2), As1-Co2-As2 69.5(1), As1-Co2-C12 93.3(4), As2-Co2-C12 97.3(4), Co1-As1-Co2 107.7(1), Co1-As1-S1 58.2(1), Co2-As1-S1 110.7(1).

The crystal structure of **5**[13] is characterized by a $Co_3As_2S_4$ cage, in which one μ_3-S and one μ_3-As_2S_3 ligand form the main constituents of a distorted cube (with As1 above a plane) (Fig. 2). The construction of the As_2S_3 bridge can be seen as a molecular section from the As_nS_{2n+1} chain

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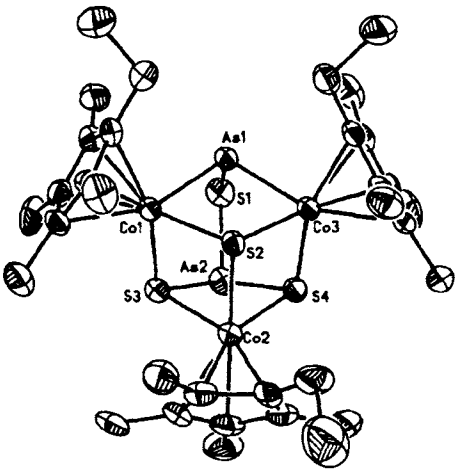

Fig. 2. Crystal structure of **5**. Selected distances [Å] and angles [ ]: Co1-As1 2.342(3), Co1-S2 2.266(4), Co1-S3 2.209(4), Co2-S2 2.274(4), Co2-S3 2.272(4), Co2-S4 2.274(4), Co3-As1 2.341(3), Co3-S2 2.263(4), As1-S1 2.318(4), As2-S1 2.196(1), As2-S3 2.292(4), As2-S4 2.292(4); As1-Co1-S2 78.5(1), Co1-As1-Co3 98.1(1), Co1-S2-Co3 102.7(1), S3-Co2-S4 89.0(1), S3-As2-S4 88.1(1), As1-S1-As2 98.0(1).

with trigonal pyramidal AsS_3 subunit[6] typical for sulfo salts; at the As1 atom two Co atoms replace two S atoms. Correspondingly, the As–S distances also vary between 2.195 and 2.318 Å. Of the noble gas-configurated Co centers, Co1 and Co3 are symmetry equivalent, which is also in accordance with the ^{1}H NMR spectrum (Table 1).

Since the reaction of **1** with As_4S_4 in boiling xylene (15 h) only affords **3** and **5** in 11 and 51% yield, respectively, it appears likely that **2** and **4** are intermediate products. Indeed, warming solutions of **2** to 110 °C affords **3** (25% yield), **4** (10%), and **5** (18-28%). Interestingly, the addition of sulfur does not cause the linkage of the two AsS ligands, rather, only the isolation of a small quantity of $[Cp^x_2Co_2S_4]$.[15]

It can be concluded that AsS units play an important role in the construction of new cage structures which are characterized by the As_2S_3 framework. A comparison with the fragmentation of the As_4 tetrahedron by **1** seems appropriate,[16] although the apparently rapid opening of the edges of the As_4S_4 framework has not been proven to date. Compound **2** is, however, structurally analogous to [Cp*Co-(μ-η^4:η^1:η^1-As_4)Co(CO)Cp*], an intermediate from this reaction, when the two S-"wing tips" are replaced by an As–As building block. Also this complex is thermally unstable. However, it rearranges into a Co_3As_6 framework, which can be described as a strongly distorted As_6 prismane constructed from three As_2 units.

Experimental Procedure

The suspension from **1** (902 mg, 1.91 mmol) and As_4S_4 (817 mg, 1.91 mmol) in toluene (50 mL) was stirred for 15 h at 80 °C. After the solvent had been removed, the oily brown residue was taken up in toluene and prepurified on SiO_2 (column 10 × 3 cm). With toluene/ether 10:1 first a very broad red-brown zone was eluted and then a brown zone which contained **2** in 10% yield. The first zone was then chromatographed on SiO_2 (column 84 × 2.5 cm). With toluene/pentane 1:1 a series of compounds was eluted: orange-red $[Cp^*Co(CO)_2]$, green-brown **4**, red-brown **5**, and finally violet **3** (yields: 13 (**4**), 11 (**5**), 6 (**3**)%). Recrystallization at −20 °C from toluene/pentane mixtures afforded brown (**2**.**4**.**5**) and dark violet (**3**) crystals, respectively.

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[7] The 48 e cluster $[Cp^*_2Mo_2AsS_3Co(CO)_2]$ contains a μ_2,η^2-AsS ligand, however this ligand is derived from the compound $[Cp^*_2Mo_2As_2S_3]$, which has not yet been confirmed structurally (H. Brunner, H. Kauermann, U. Klement, J. Wachter, T. Zahn, M. L. Ziegler, *Angew. Chem.* **1985**, *97*, 122; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*,132).

[8] Correct C, H, S elemental analyses. FD mass spectra (toluene) **2**: *m/z* 658.2 ($M^{\oplus}$); **3**: *m/z* 662.3 ($M^{\oplus}$); **4**: *m/z* 988.7 ($M^{\oplus}$); **5**: *m/z* 902.5 ($M^{\oplus}$).

[9] Compound **2** crystallizes in the form of brown plates, which contain half a molecule of toluene (disordered) per formula unit. Space group $C2h/5$-$P2_1/n$ (no. 14), a = 9.046(4), b = 26.01(1), c = 12.636(5) Å, β = 99.59(3)°, V = 2931.5 Å^3 (25 reflections ($3.0 < 2\theta < 19.0$°)); Z = 4. Syntex-R3 diffractometer ($Mo_{K\alpha}$), $3.0 < 2\theta < 52.5$°; 6069 reflections, of which 2537 with $I > 2.5\sigma(I)$ were used for the refinement. Decrease in intensity of the reference reflections during the measurement balanced up to 55% by corresponding correction of the intensities. Patterson and Fourier methods, anisotropic refinement to R = 0.073, R_w = 0.055 [14].

[10] As–As bonds in transition metal complexes lie in the range 2.273(3)–2.445(4) Å [1a]. However, distances of 2.57 and 2.76 Å have also previously been discussed as being of bonding nature (A. L. Rheingold, M. J. Foley, P. J. Sullivan, *J. Am. Chem. Soc.* **1982**, *104*, 4727).

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[13] **5** crystallizes in the form of thin, long plates of the dimensions 0.05 × 0.15 × 0.7 mm^3. Space group $C2h/5$, $P2_1/n$ (no. 14), a = 8.849(3), b = 21.81(2), c = 19.54(2) Å, β = 96.24(6)°, V = 3748.8 Å^3 (16 reflections ($4.3 < 2\theta < 14.8$°)), Z = 4. Syntex-R3 diffractometer ($Mo_{K\alpha}$), $3.0 < 2\theta < 47.5$°; 5878 reflections, of which 2867 with $I < 2.5\sigma(I)$ were used for the refinement. Empirical absorption correction. Patterson and Fourier methods, anisotropic refinement to R = 0.060, R_w = 0.048 [14].

[14] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-57465, the names of the authors, and the journal citation.

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The First Heteroallyl Metal Complexes of Arsenic with the Coordination Number 2**

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Dedicated to Professor Helmut Werner on the occasion of his 60th birthday

The chemistry of low-coordinate group 15 elements of the periodic table has already been the subject of numerous investigations. Particular emphasis was focused on phosphorus compounds such as phosphaalkynes and -alkenes,[1] diphosphenes,[2] and iminophosphanes.[3] These compounds have already been used as synthetic building blocks.[1–4] In contrast, the chemistry of compounds containing low-coor-

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